REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
03-24-2004	Technical Paper (View Graph)	

4. TITLE AND SUBTITLE

Polynitrogen Chemistry: Recent Development in Pentazole and Polyazide Chemistry

5a. CONTRACT NUMBER
F04611-99-C-0025

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Ashwani Vij, Vandan Vij, R. Haiges, Karl O. Christe

5d. PROJECT NUMBER
DARP

5e. TASK NUMBER
A205

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

ERC Incorporated
555 Sparkman Drive
Huntsville, AL 35816-0000

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRSB
4 Draco Drive
Edwards AFB CA 93524-7160

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
AFRL-PR-ED-VG-2004-088

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

American Chemical Society Meeting (ACS) National Meeting
Anaheim, CA 28 Mar – 01 Apr 2004

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Linda Talon
Unclassified	Unclassified	Unclassified	A	38	19b. TELEPHONE NUMBER (include area code) (661) 275-5865

Polynitrogen Chemistry: Recent Development in Pentazole and Polyazide Chemistry

Ashwani Vij
Space and Missile Propulsion Division
Air Force Research Laboratory/PRSP
Edwards AFB, CA 93524
ashwani.vij@edwards.af.mil
(661) 275-6278

Inorganic Division, 227th National ACS Meeting, Anaheim-CA, April 1, 2004

Why Polynitrogen Compounds ?

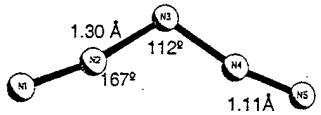
- Polynitrogen compounds contain only nitrogen atoms and are expected to have unusual properties. Most important among these are:
  - *High endothermicity*
  - *"Green" propellant*

    "combustion" product is only gaseous N_2
  - *High density*
  - *High I_{sp} values when compared to other monopropropellants or bipropellants*

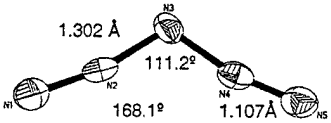
High detonation velocity

Geometry of the N_5^+ cation

V-Shaped Geometry

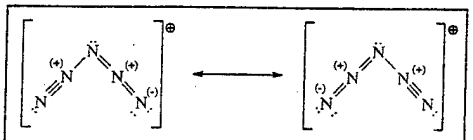


Calculated Structure

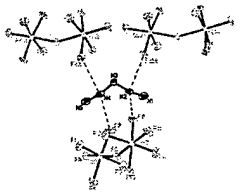


Experimental Structure

Vij, Wilson, Vij, Tham, Sheehy & Christe, *J. Am. Chem. Soc.*, **2001**, *123*, 6308-6313



Resonance Structure



N2 makes contacts at 2.723 and 2.768 Å

N4 contacts are at 2.887 and 2.814 Å

C&E News, 2000, *78*, 41

(In)Compatability of N_5^+

Attempts to couple N_5^+ with energetic anions can result in explosive reactions !!!

$N_5^+N_3^-$

$N_5^+ClO_4^-$

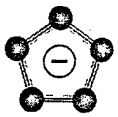
$N_5^+NO_3^-$

$N_5^+N(NO_2)_2^-$

Our goal is the synthesis of an "aromatic" polynitrogen anion with

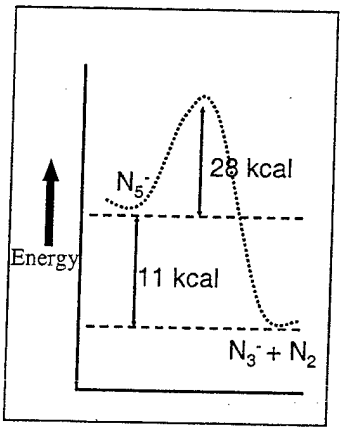
- *A high first ionization potential*
- *A high activation energy barrier towards decomposition*

New Polynitrogen Anions as Counterparts for N_5^+



Pentazole anion (N_5^-)

- *Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to N_3^- and N_2 is only 11 kcal/mol exothermic*
- *Free pentazole has not been isolated to date. Only aryl substituted pentazoles can be isolated and stabilized at low temperatures. These compounds rapidly decompose above 273K to form aryl azides and N_2 gas*

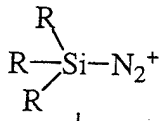


Synthetic Challenge – How do we make These New Anions??

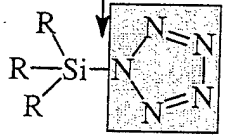
Synthesis of Substituted Pentazoles

Sources for the Pentazole Anion (N_5^-)

Silyl Diazonium Salts

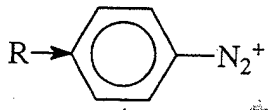


$+N_3^-$



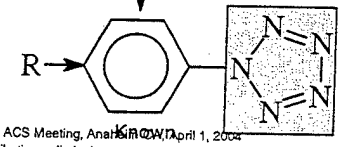
Unknown

Aryl Diazonium Salts



R = electron releasing group

$+N_3^-$



Known

T. Ugi, *Angew. Chem.*, 1961, *73*, 172

Formation and Stability of Silyl Diazonium Salts

- Failed attempts to synthesize silyl diazonium salts

$$N_2F^+SbF_6^- + Me_3SiSiMe_3 \xrightarrow{-Me_3SiF} Me_3SiN_2^+SbF_6^-$$

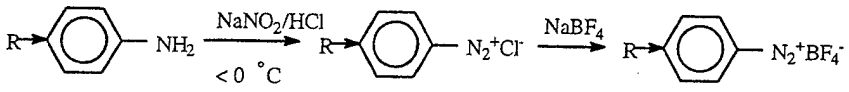
- $R_3SiN_2^+$ salts are unstable and spontaneously lose N_2

$$R_3SiN_2^+ X^- \xrightarrow{-N_2} \left[R_3Si^+ X^-\right]$$

Theoretical calculations support this experimental observation

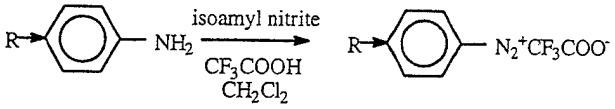
Synthesis of Aryldiazonium Salts

Aqueous Media

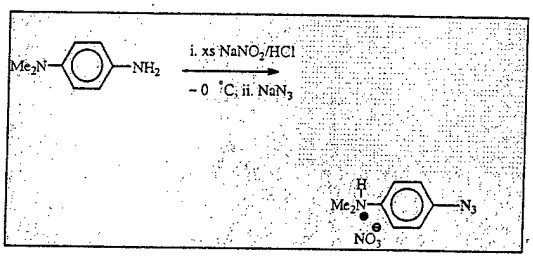


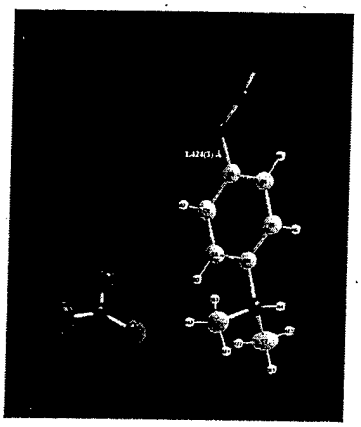
R = H, OH, OCH_3, OC_6H_5, $OC_6H_4N_2^+$, $N(CH_3)_2$

Non-aqueous Media



Pentazole Formation... Not a Trivial Chore !!!





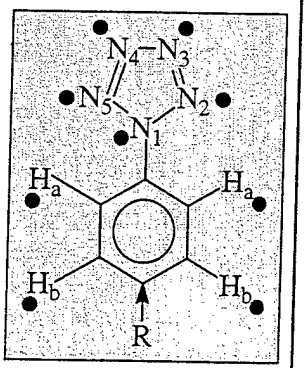
$$NaNO_2 + HCl \xrightarrow{< 0\ ^\circ C} NaCl + HONO$$

$$3\ HONO\ (aq) \rightleftharpoons H_3O^+ + NO_3^- + 2NO$$

Identification of Arylpentazoles

Pentazoles can be characterized by low temperature NMR spectral studies using ^{15}N labeled samples.

- **^{1}H NMR:** *AB*-type spectrum with H_a and H_b at 8.0 and 7.0 ppm
- **^{14}N NMR:** N_1 at ~ -80 ppm
- **^{15}N NMR:** N_2/N_5 at ~ -27 ppm and N_3/N_4 at ~4 ppm

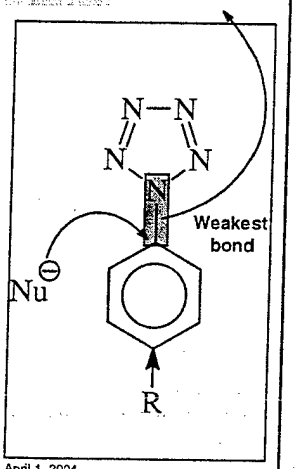


Note: Qualitative evidence for the presence of a pentazole ring: N_2 gas evolution in solution

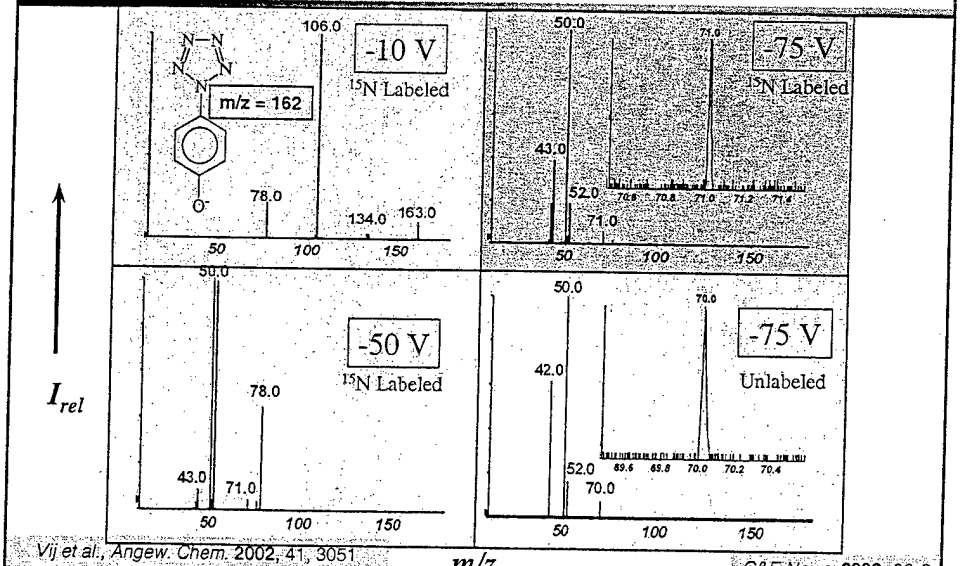
Cleavage of the Aryl-Pentazole Bond with Retention of the Pentazole Ring

- **Chemical Methods**
  - Ozonolysis does not work! (Ugi, Radziszewski)

    V. Benin, P. Kszynski and G. J. Radziszewski, *J. Org. Chem.*, 2002, *67*, 1354
  - Nucleophilic substitution using strong nucleophiles such as the OH^-, OR^-, F^- etc.
- **Collisional Fragmentation** (ElectroSpray Ion Mass Spectroscopy – **ESIMS**)
  - Electrospray is very gentle and produces high concentration of the parent anion which can be mass selected
  - Negative ion detection eliminates interference from neutral or positively charged species



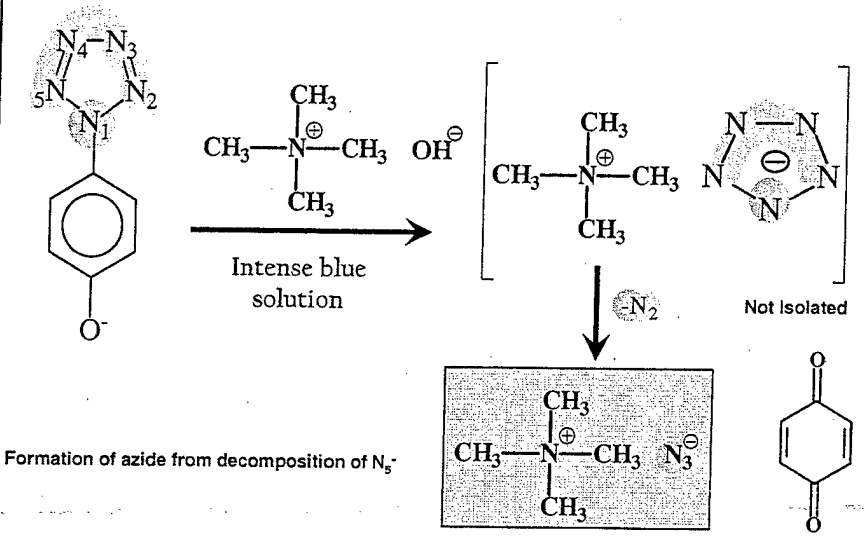
MSMS of the Parent Ion Peak



Vij et al., Angew. Chem. 2002, 41, 3051

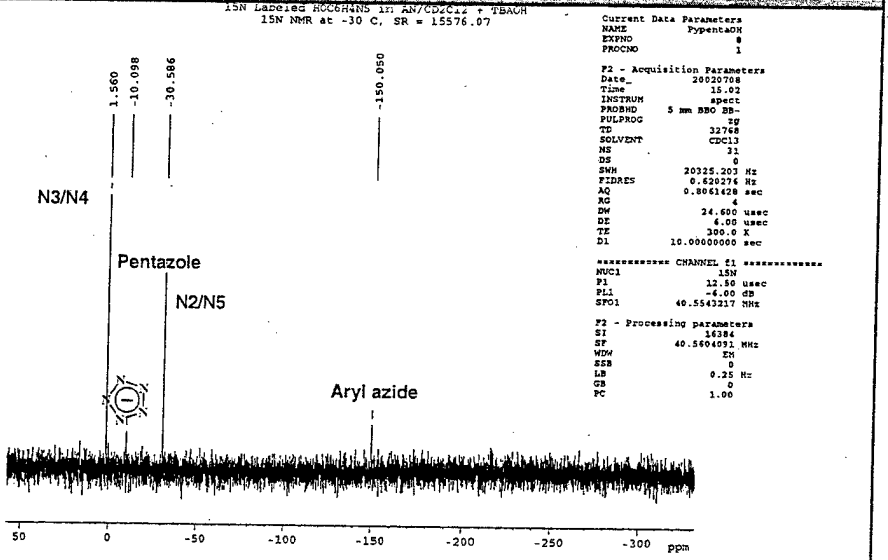
C&E News, 2002, *80*, 8

Chemical Cleavage of the C-N Bond

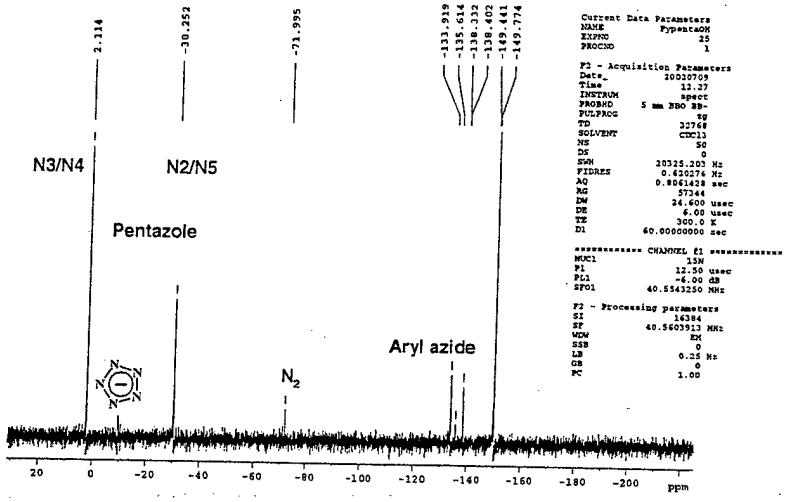


Formation of azide from decomposition of N_5^-

Aryl-pentazole bond cleavage: N_5^- anion in Solution

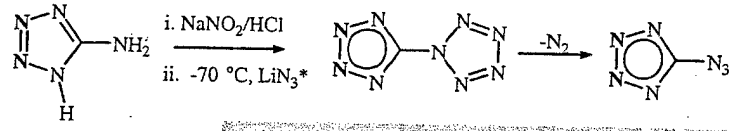


Subsequent Decomposition of the Pentazole Anion



Pentazoles with Heterocyclic Substituents

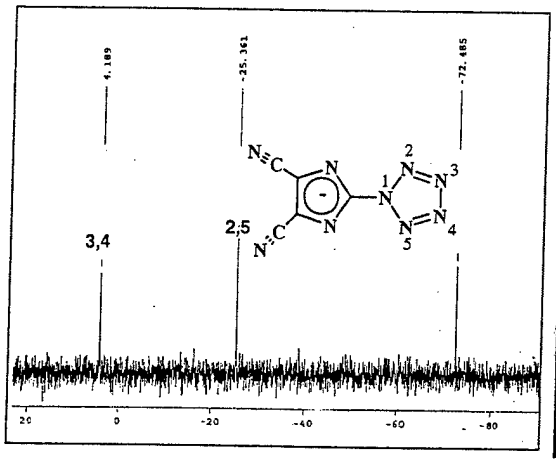
- Tetrazolyl system is unstable above -70 °C and the pentazole ring rapidly decomposes to liberate N_2 gas.

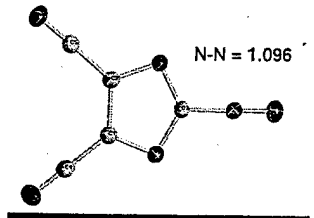


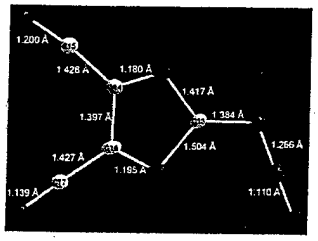
A. Hammerl and T. M. Klapoetke, *Inorg. Chem.* 2002, *41*, 906-912

- In comparison, the pentazole ring derived from 2-amino-4,5-dicyanoimidazole shows higher thermal stability (-30 °C)

^{15}N NMR of 2-pentazolyl-4,5-dicyano-imidazole

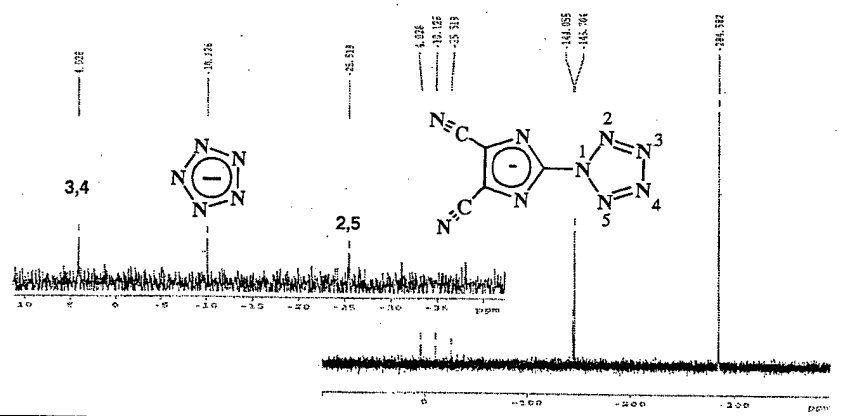






^{15}N NMR recorded in a mixture of methanol and acetonitrile at -30 °C, nitromethane used as an external reference (0 ppm)

Pentazolate Anion in Solution ?



- ^{15}N NMR shows a peak at ~ -10 ppm (-30 °C) upon addition of base, which slowly decomposes to form N_2 and azide ion.
- This peak is also observed upon adding a base to the solution of arylpentazoles at -30 °C.

Chronology of the Pentazolate Anion

- ESIMS of *para*-hydroxyphenylpentazole

  Vij, Pavlovich, Wilson, Vij, Christe, Angew. Chem. Intl. Ed. Engl 2002, 41, 3051
  Submitted: April 30, 2002; accepted July 3, 2002

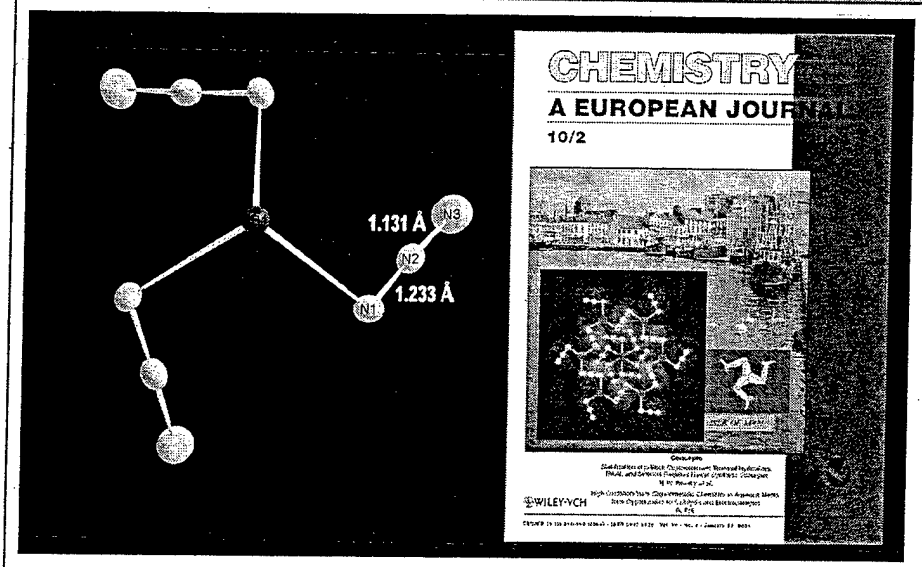
- ^{15}N NMR studies showing a peak at -10.2 ppm (-40 °C) due to the Pentazole anion resulting from cleavage of *para*-methoxyphenylpentazole which slowly decomposes to form N2 and azide ion. Upon standing for several days, all peaks dissappear!

  Butler, Stephens & Burke, Chem. Commun. 2003, 1016
  Submitted: February 6, 2003; accepted February 27, 2003

- Laser Desorption Ionization (LDI) time-of-flight (TOF) mass spectrometry of solid *para-N,N*-dimethylaminophenylpentazole shows peaks at m/z: 70 (N_5^-) and -42 (N_3^-). Peak at 70 confirmed by ^{15}N labeling experiment.

  Ostmark, Wallin, Brinck, Carlqvist, Claridge, Hedlund & Yudina,
  Chem. Phys Lett., 2003, 379, 539
  Submitted: Jun. 27, 2003; accepted August 27, 2003

What are "normal" N-N distances in azides?



Abnormalities in azide distances: Artifacts or Structural Contaminants?

- ✓ A large number of crystal structures reported in Cambridge/Inorganic CSD report unusually short N_α-N_β (0.8- 1.0 A) and long N_β-N_γ (1.2-1.4) distances. According to VB theory, in covalently bonded azides, N_α-$N_\beta > N_\beta$-N_γ

  Wolfgang, F. and Klapoetke, T. In Inorganic Chemistry Highlights, Meyer, G., Naumann, D. and Wesemann, L. Eds.; Wiley-VCH: Weinheim, 2002, Chapter 16 *and references therein*

- ✓ In most cases, these derivatives were prepared from metal chloride salts and/or recrystallized from chlorinated solvents

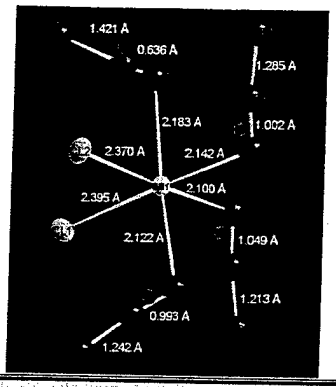
Reactivity of hexachloroantimonate (VI) with Trimethylsilylazide

$$[Ph_4M][SbCl_6] + Me_3SiN_3 \xrightarrow[CH_3CN,\ 60\ ^\circ C]{-Me_3SiCl} [Ph_4M][SbCl_{6-x}(N_3)_x]$$

M = P, As; x = 2-6

- ✓The substitution of all the six chlorine atoms in $SbCl_6^-$ by the azide groups could not be accomplished in a single step, as reported in literature. The stepwise substitution gives a good insight into the substitution mechanism.
- ✓ Total substitution was achieved after four "refreshment" cycles of the reagents. During the intermediate cycles, the azide content gradually increased from two to five.

The tetraphenylarsonium antimonychloride azide case



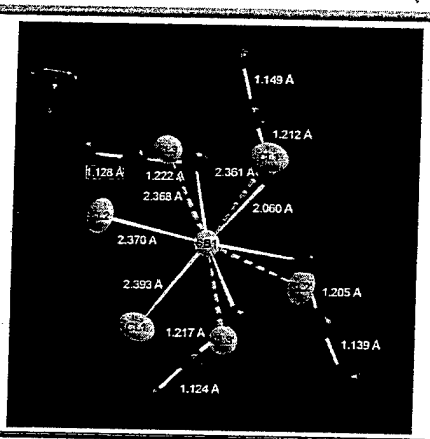
Orthorhombic, $P2_12_12_1$

a, b, c ( ) =7.7744(14), 13.610(3), 27.094(5)

V = 2866.8(10), Z = 4

R = 3.22%, S = 1.088, highest peak = 0.58 e/ ^{3}

Flack's parameter = 0.03(1)



Chloride contamination (%)

N1-N3 = 10; N4-N6 = 18; N7-N9 = 16; N10-N12 = 37

R = 3.22%, S = 1.088, highest peak = 0.58 e/ ^{3}

Flack's parameter = 0.03(1)

Summary

- Synthesized aryl pentazoles: hydroxy group at the *para*-position on the aryl ring gives the best results as observed during this study.
- Demonstrated selective cleavage of C-N bond by ESIMS with retention of pentazole ring. Results confirmed studying ^{15}N labeled pentazoles.
- Experimental detection of pentazolate anion in solution using different substrates.
- Offers potential pathway for bulk synthesis of N_5^- salts
- Chloride ion cause abnormalities in N-N bonds in azides

Acknowledgments

Dr. Karl Christe, Dr. William Wilson, Ms. Vandana Vij (ERC Inc.)

Dr. Gregory Drake (AFRL)

Dr. Ralf Haiges (USC)

Dr. Fook Tham (UC Riverside)

Dr. James Pavlovich (UCSB)

Dr. Robert Corley, Dr. Ronald Channell, Mr. Michael Huggins (AFRL)

$$$

Dr. Don Woodbury, Dr. Arthur Morrish (DARPA)

Dr. Michael Berman (AFOSR)

BACKUP

Recipe for Synthesizing Neutral Polynitrogen Compounds

- Combine a polynitrogen cation with a polynitrogen anion to form a neutral polynitrogen compound.

$$N_x^+ + N_y^- \longrightarrow N_{x+y}$$

ONLY TWO STABLE POLYNITOGEN IONS KNOWN TO EXIST IN BULK

Cation

N_5^+ cation

(discovered in 1999, AFRL, Christe)

Anion

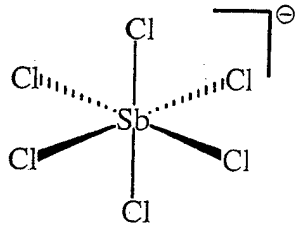
N_3^- anion

(discovered in 1890, Curtius)

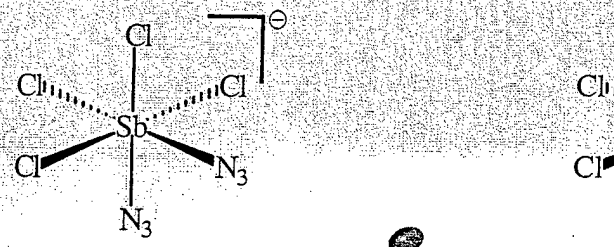
Episode I...Generation of the starting material

$$Ph_4MCl + SbCl_5 \xrightarrow{1,2\text{-DCE}} [Ph_4M][SbCl_6]$$

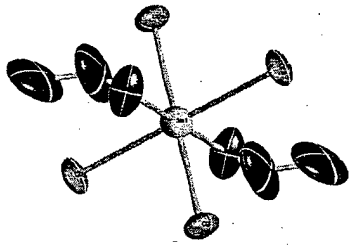
M = P, As

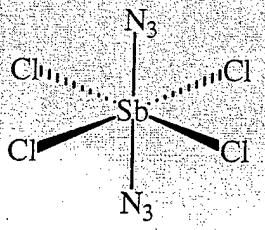


Episode II....cis- or trans- disubstitution with azide groups?



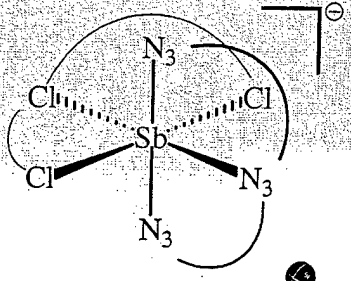
cis-isomer

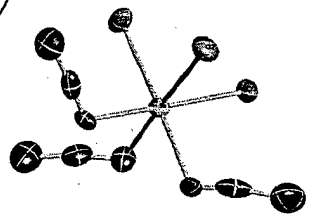




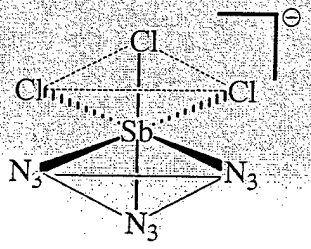
trans-isomer

Episode III...Substitution of 3rd chlorine... fac- or mer- isomer ???





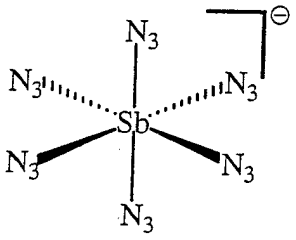
mer-$SbCl_3(N_3)_3$



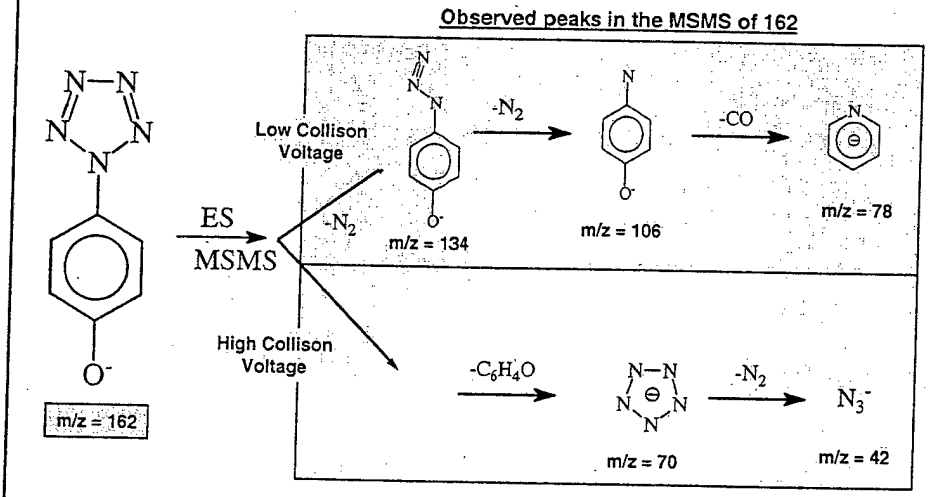
fac-$SbCl_3(N_3)_3$

Episode VI...Complete substitution of chlorine atoms

No crystal structure obtained yet. However, IR and Raman spectroscopy shows that Sb-Cl bonds are absent i.e., complete substitution by the azide groups.

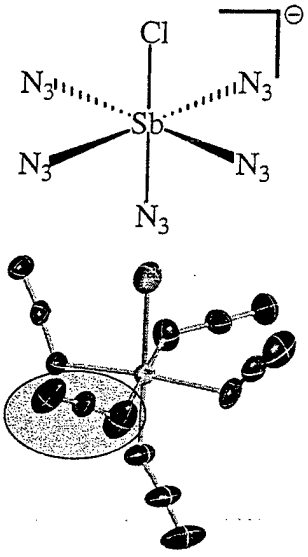


ESIMS of para-Phenoxypentazole



Vij, Pavlovich, Wilson, Vij & Christe, *Angew. Chem. Int. Ed.*, 2002, *41*, 3051-3054

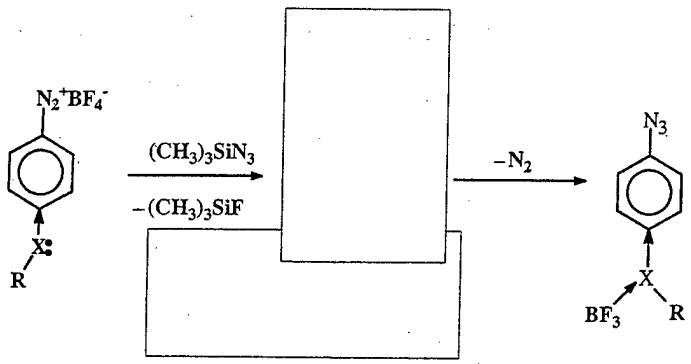
Episode V: Synthesis of Chloropentaazidoantimonate(VI) Anion



The Structure of $Ph_4PSbCl(N_3)_5$

- ✓ The crystals grown from CH_3CN
- ✓ *Triclinic* space group *P-1*
- ✓ Cell constants: *a = 11.134(3) Å , b = 11.663(3) Å, c = 13.754(4) Å; α = 104.314(5)º; β = 97.914(5)º; γ = 115.807(4)º*
- ✓ *Z = 2*
- ✓ *R = 0.0762*
- ✓ *All azide distances "normal" except N10-N11-N12*

Reaction with Trimethylsilyl Azide



X= N, O

No pentazoles were isolated !!!

Reactions carried out in acetonitrile at -30 °C